External dry hopping: the solution for problems? (Part 2)

BEER ANALYSES TEST BEERS | During dry hopping, extraction of hop aroma poses multiple challenges for brewers, as has been described in Part 1 of this series of articles. In this second part of the series of articles, a method on a laboratory scale is presented in which extraction of hop aroma is carried out by re-dilution.

PART 1 OF THIS SERIES of articles described the chemical-physical background of the new development of a dry hopping method [1]. The preliminary tests detailed in Part 1 already pointed to the fact that mass transfer of hop aroma components is impeded or restricted with increasing mass concentration of hop components. However, when the highly concentrated suspension was diluted with beer, directly followed by filtration, mass transfer of hop aroma components impeded could be immediately restored. Based on the results of the preliminary tests, further tests were carried out to confirm the results. We will take a closer look at them here.

Test setup

The Citra® hop variety was selected for the tests as it is available all over the world and is frequently used for dry hopping [2]. BBC Pure Hop Pellet™ (BBC) was the hop product of choice for the tests. Tests using T90 and Lupomax pellets were are also carried out yielding comparable results.

The base beer used was an unpasteurised, unfiltered lager beer that had not been dry hopped, brewed by a commercial brewery and having an ABV of 5.3 %v/v, 14 mg of iso-alpha-acids and a pH of 4.57.

A dispersion/stirring time of 120 min was chosen in order to assure complete dispersion of the hop pellets into hop powder and initiate transfer of hop ingredients into the beer. The suspension temperature was set at 15 °C because, according to a survey by McIlmoyle et at. [3], dry hopping in breweries is usually carried out at that temperature. Fig. 1 shows preparation of samples.

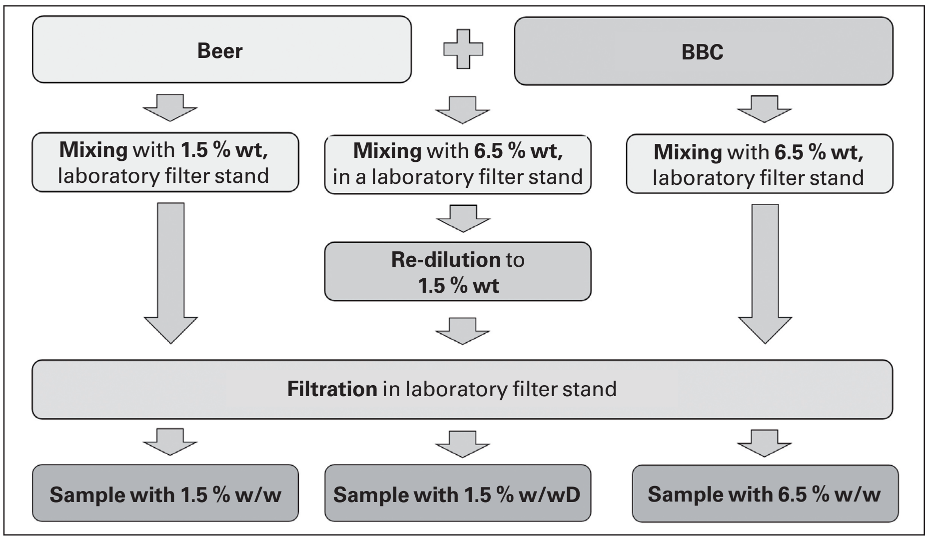

Fig. 1 Overview of tests carried out

To reduce the number of samples, mixed samples containing terpenes, esters and thiols from three individual samples prepared independently of each other were analysed. This method had been verified and found conclusive in separate individual analyses beforehand.

Beer analyses

Hop bitter substances were analysed according to EBC 9.50 [4]. Terpenes and terpeniods were analysed according to the HS-SPME-GC-MS/MS method developed by Johanna Dennenloehr et al. [5]. Thiols were analysed using a gas chromatograph. The method used has been presented by Nils Rettberg et al. at the EBC Symposium "Recent Advances in Hop Science" in 2018 [6].

Test results

Hop bitter substances

Data in fig. 2 shows that dry hopping resulted in a reduction of the concentration of iso-alpha acids in all tests. This effect has

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been presented by John Paul Maye et al. in 2016 [7].

Concentration of iso-alpha acids falls more sharply in the sample with 6.5 %w/w (by 8.83 mg/l) compared to the reference sample with 1.5 %w/wD (by 4.93 mg/l) and the sample with 1.5 w/w (by 3.07 mg/l). This can be attributed to the fact that about a fourfold quantity of hop material was added to the suspension in the sample with 6.5 %w/w. As iso-alpha acids are slightly soluble in water and have surface-active properties, a larger quantity of iso-alpha acids, together with hop solids, was separated from the suspension in the presence of more plant material. However, the drop in iso-alpha acids in the highly concentrated sample with 6.5 %w/w is the lowest one of the three samples based on 100 g/hl. The value is 0.14 based on 100 g of hop pellets added per hectolitre.

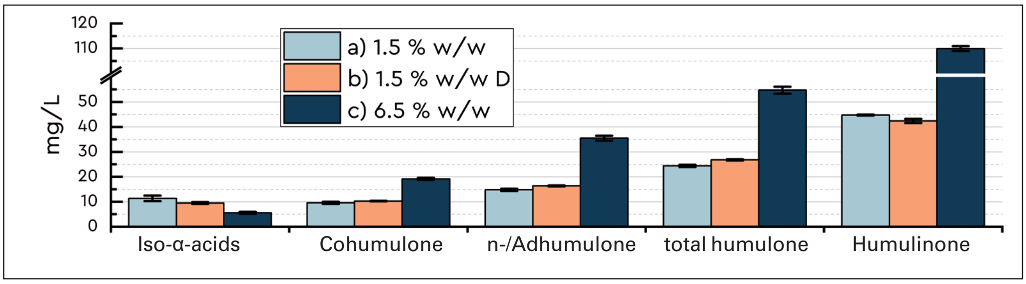

Fig. 2 Results of analysis of bitter substances

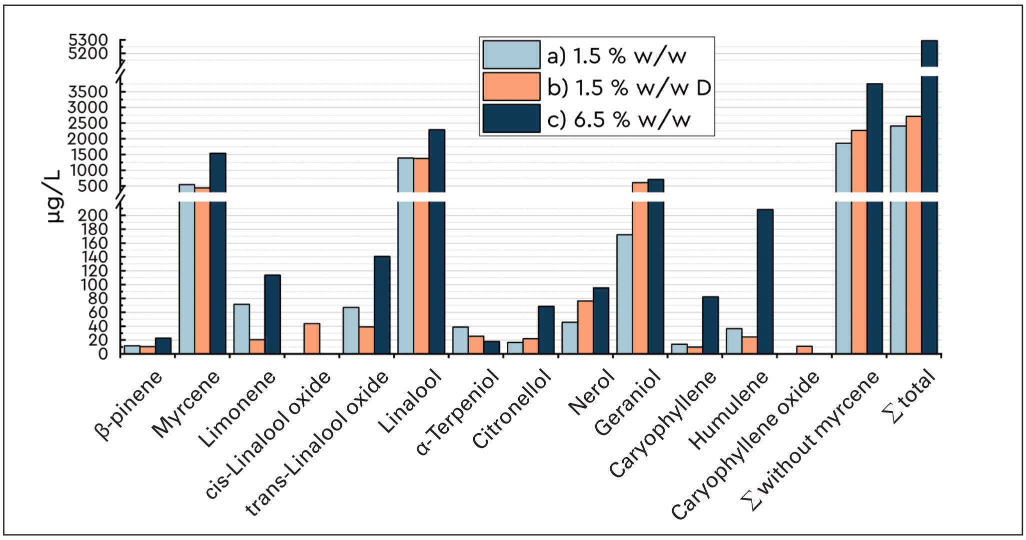

Fig. 3 Results of terpene analysis

The data in fig. 2 shows a rise in humulones and humulinones in all samples compared to the concentrations measured in the base beer. This was previously also reported by Maye et al. in 2016 [7].

No measurable concentration of humulones and just a small quantity of humulinones of 1.67 mg/l were found in the base beer. This is due to the slight solubility of humulones at low pH values [8].

No significant difference was noted for any analyte when comparing the 1.5 %w/w and 1.5 %w/wD samples. In other words: the quantity of hops as such added has an effect on bitter substances.

pH value

In all tests, addition of hops resulted in a pH increase. An identical absolute increase in pH of 0.2 was measured in the two 1.5 wt % samples with and without dilution. This corresponds to 0.014 per 100 g/hl. Increase in pH in the 6.5 wt % sample was 0.43, about twice as much, corresponding to a specific increase in pH of just 0.0007 per 100 g/hl.

In summary, no significant differences between the two techniques, based on the change of pH, were noted.

Terpenes

Generally, concentrations of terpenes in the samples with 6.5 % w/w are higher than those in the two samples with 1.5 % w/w (fig. 3). However, terpene concentration does not rise proportionally when more hops are added.

This confirms that, at high hop concentrations, phenomena set in that inhibit mass transfer of aroma substances into the beer medium [9].

Caryophyllenes and humulenes do not seem to be affected by inhibiting effects on mass transfer. Their concentrations in the 6.5 % w/w sample are 82.4 µg/l and 208.5 µg/l, thus clearly higher than in the 1.5 % w/w samples. Scott Lafontaine and Thomas Shellhammer were able to measure this effect also in static dry hopping tests [9].

A comparison between the 1.5 % w/w samples with 1.5 % w/wD samples shows that dilution does not seem to have disadvantages for yield of terpenes. This in particular applies to linalool with concentrations of 1389.9 µg/l and 1378.8 µg/l, to myrcene of 544.8 µg/l and 443.2 µg/l and also to beta-pinene of 11.5 µg/l and 10.6 µg/l. Quantities measured are quite similar when taking account of standard measurement errors of analysis methods. Geraniol is an exception, its concentration of 608.4 µg/l in the sample with 1.5 %w/wD is similar to that of 710.3 µg/l in the sample with 6.5 %w/w. However, geraniol concentration in the 1.5 %w/w is only 172.2 µg/l.

Differences between the two samples with 1.5 % wt are small when considering the total concentration of terpenes.

Esters

The esters shown in fig. 4 follow a pattern similar to that of terpenes. Values measured in the 1.5 % w/wD sample and the 1.5 % w/w sample are comparable. However, differences between the concentrations of isobutyl isobutyrate ethyl isobutyrate (155.2 µg/l and 24.3 µg/l) in the 1.5 % w/w sample compared to the same esters in the 1.5 % w/wD sample (106.7 µg/l of isobutyl isobutyrate and 15.5 µg/l of ethyl isobutyrate) were measured.

Values measured for all esters in the sample with 1.5 wt % hardly differ when considering the whole terpene group.

Values measured for all esters were higher in the sample with 6.5 wt %. However, they do not reflect the much higher addition of more than the fourfold quantity of

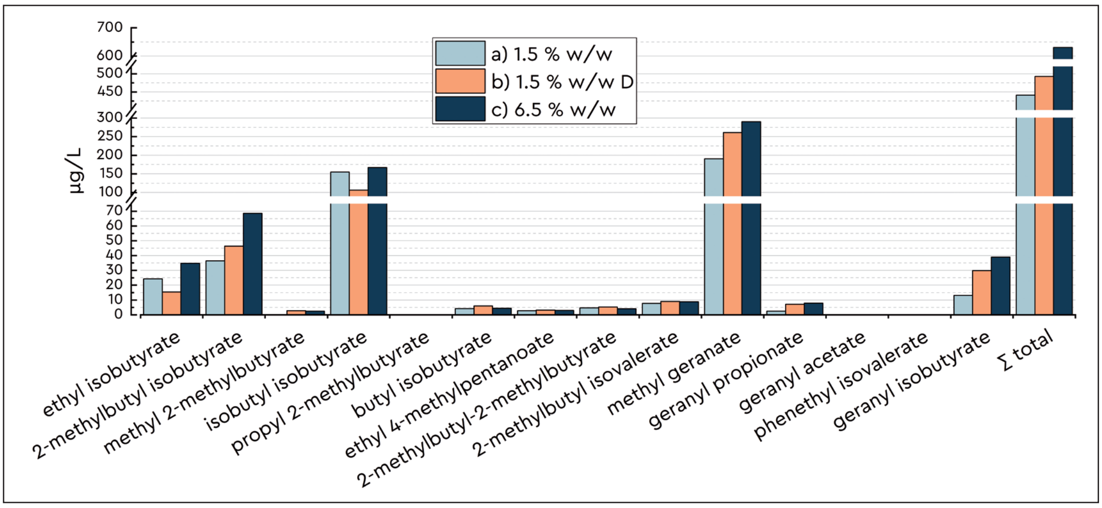

Fig. 4 Results of ester analysis

TRANSFER RATES OF SELECTED HOP COMPONENTS

Transfer rates	Linalool	Limolene	Geraniol	Nerol	Humulione	4MMP
1.5 % w/w	53	14	13	17	57	46
1,.5 % w/wD	52	4	44	28	54	115
6.5 % w/w	20	5	12	8	33	79

Table 1

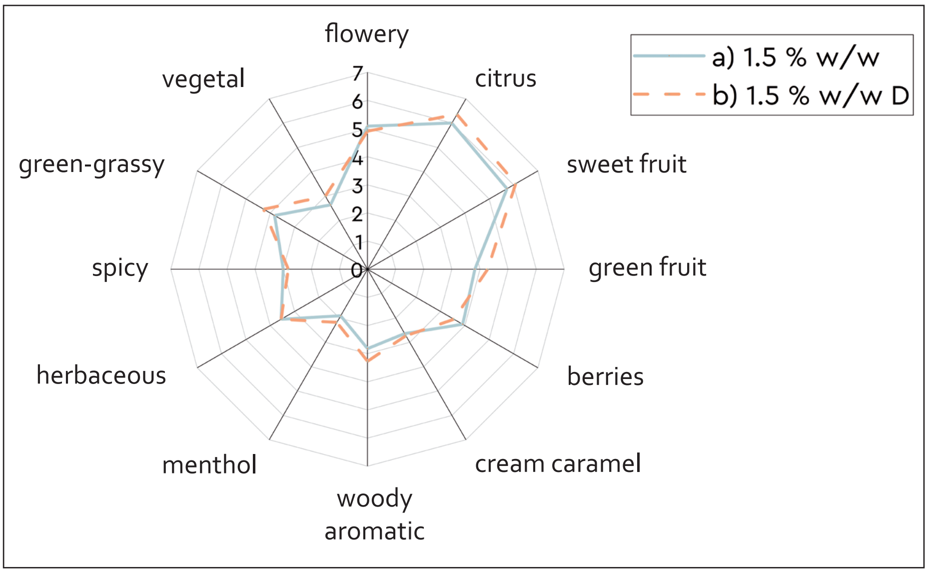

Fig. 5 Results of sensory assessment of intensity of hop aromas

hops. As has been observed for terpenes, mass transfer of hop compounds into the beer matrix seems to be inhibited at higher concentrations of esters.

However, the total sum of esters differs insignificantly between the two samples.

Thiols

Values for 4-MMP and 3-MH analysed in the sample with 6.5 % w/w were clearly higher than the values measured in the samples with 1.5 % w/wD and 1.5 % w/w. Apparently, the higher thiol concentrations correspond to some extent to the higher hop addition. As opposed to terpenes and esters, mass transfer of thiols was not inhibited at such higher hop concentrations.

When comparing the 1.5 % w/w samples, the 1.5 % w/wD sample having a concentration of 55.0 mg/l contains higher quantities of 4-MMP than the 1.5 % w/w sample with 22.2 ng/l. For 3-MH, the concentration of 30.7 ng/l is somewhat higher than in the 1.5 % w/w sample.

Total thiols of 52.9 ng/l and 73.9 ng/l are very close to each other and point to a slight difference between the 1.5 % w/w samples considering the standard deviation of the analysis method.

Transfer rates

Transfer rates of linalool into the two 1.5 % w/w samples of 52 per cent and 53 per cent are almost identical (see table 1). In contrast, the sample with 6.5 % w/w shows a clearly lower yield of 20 per cent. This confirms that percentage mass transfer is clearly lower with increasing mass concentration. This effect has also been observed for nerol and humulinones. No clear-cut results were measured for limonene, geraniol and nerol.

Sensory analysis

In addition to laboratory analysis, samples were evaluated by a trained taster panel for confirmation and validation. A discriminatory as well as a descriptive test of the undiluted 1.5 % w/w and the diluted 1.5 % w/wD (reference) samples were carried out.

A triangle test according to DIN EN ISO 4120:2007-10 [10] was used for the discriminatory test and the Hopsessed® Assessment Scale from BarthHaas, Nuremberg, for the descriptive tasting. For the latter, hop aromas were subdivided into twelve general categories and assessed on a scale from 0 to 10 [11].

In addition to aroma and taste attributes, the panel members (n=10) assessed six attributes in order to classify hop quality in the beer.

Discriminatory test

The test resulted in no significant difference between the two production methods. Five samples were correctly identified up to a value of $\alpha = 0.20$. Though the result does not unequivocally confirm the similarity of samples, it shows a trend into a certain direction which was confirmed by the results of descriptive tasting.

Descriptive test

The descriptive taste test indicated that the scoring results did not shows any significant difference within each category when tested by well trained tasters. Fig. 5 shows a spider diagram of the results for the sample with 1.5 % w/wD and the sample with 1.5 % w/w.

This confirms the results of the discriminatory test i.e. that there is no conceivable difference between the two samples.

The spider diagram in fig. 6 shows that assessment of intensity of bitterness and quality of hop aroma was also almost identical. No significant difference between the two samples was found for any of the attributes, the significance level was 0.05. This could also be confirmed by the bitterness perceived. The difference between the 1.5 % w/wD sample with 35.09 ± 5.19 bitter units (BU) and the 1.5 % w/w sample with a value of 34.55 ± 4.59 BU was just 0.54 BU.

All results of the sensory assessment confirm that there is no significant difference between the two production methods.

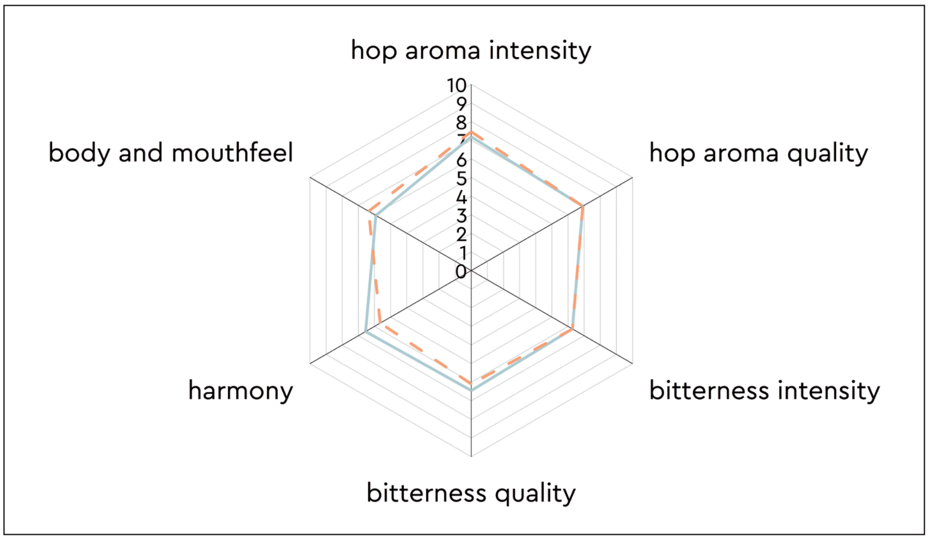

Fig. 6 Results of sensory assessment of bitterness

Outlook

In Part 3 of this series of articles, a dry hopping system developed for industrial use will be presented and impressions and experience from the first plant on a scale of 100 – 3500 kg will be described. Part 3 will also summarise the results of the series of articles. ■

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